



Catalysts to improve the abatement of sulfamethoxazole and the resulting organic carbon in water during ozonation

Fernando J. Beltrán^{*}, Pablo Pocostales, Pedro M. Álvarez, Francisco López-Piñeiro

Departamento de Ingeniería Química y Energética, Universidad de Extremadura, Avenida de Elvas S/N, 06071 Badajoz, Spain

ARTICLE INFO

Article history:

Received 24 March 2009

Received in revised form 23 July 2009

Accepted 3 August 2009

Available online 8 August 2009

Keywords:

Ozone

Sulfamethoxazole

Activated carbon

Perovskites

Alumina

Cobalt oxides

Catalytic ozonation kinetics

ABSTRACT

Sulfamethoxazole (SMX), one pharmaceutical compound, has been treated in aqueous solutions with catalysts (copper and cobalt type perovskites and cobalt–alumina) and promoters (activated carbons). Hydrogen peroxide and saturated carboxylic acids were identified as intermediates. The effects of adsorption and pH have been investigated. Removal of the starting SMX accomplished with ozone alone is a fast process but catalytic or promoted ozonation is needed to significantly reduce the resulting organic carbon. SMX is, thus, mainly removed through direct ozone reaction while hydroxyl radical oxidation is the mechanism of removal the remaining TOC. The kinetics of the process has also been investigated. Perovskite catalytic ozonation resulted to be a chemical control process and apparent rate constants for homogeneous and heterogeneous ozonation were determined. For activated carbon ozonation, external diffusion of ozone to solid particles controlled the process rate.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation systems to remove from water emergent contaminants (EC) such as pharmaceutical compounds, personal care products, etc., potentially considered as endocrine disrupting chemicals [1], are likely the most appropriate destructive technologies. Literature already reports multiple examples of the use of these technologies mainly involving ozone, UV radiation, photocatalysts, hydrogen peroxide, etc., and combinations of these agents to remove EC from water [2,3]. Among these technologies, catalytic and promoted ozonation or the use of ozone combined with catalysts or promoters of ozone decomposition in free radicals is becoming an attractive research subject that allow high transformation of the organic matter resulting from oxidation intermediates into inorganic carbon, that is, mineralization [4]. Thus, catalysts formed from cobalt oxides or perovskites (lantanates of transition metals) [5–8] and promoters such as activated carbons [9–14] have been reported very effective for reducing the organic matter from the oxidation of EC and other organic compounds.

Sulfamethoxazole (SMX), (see Fig. 1 for structure), a sulfonamide type synthetic antibiotic usually found in municipal wastewaters [15–17] is very often chosen as model EC to check the

performance of different advanced oxidation and photolytic processes [3]. Thus, SMX has been treated with ozone to check its reactivity with this oxidant [18,19] and determine the rate constant of the reaction with different methods [20–24]. Also, SMX ozonation has been studied to remove the antibacterial activities of ozonated SMX samples with good results [23]. In addition to ozonation alone, photolytic processes (photolysis alone or combined with different agents) have been the most studied systems to remove SMX from water. Thus, Boreen et al. [25] used 295–340 nm UV radiation to determine the quantum yields of SMX photolysis at different pH (between 2.6 and 10). Huber et al. [19] and Dodd et al. [23] applied UV radiation of different wavelength combined with hydrogen peroxide to determine the rate constant of the hydroxyl radical–SMX reaction and to remove antibacterial activities of sulfonamide drugs, respectively. Also, pulse radiolysis combined with absorption spectroscopy and HPLC have been applied to determine the hydroxyl radical–SMX reaction rate constant [26]. SMX TiO₂ photocatalytic oxidation has also been studied [27–29]. In these cases, Andreozzi et al. [27] found incomplete elimination of SMX in a mixture with other six EC while Hu et al. [28] observed nearly complete conversion of 100 µg L^{−1} SMX in about 60 min with UVA ($\lambda > 324$ nm) and TiO₂. In this latter case, approximately 80% mineralization was also observed after 300 min reaction. The authors also identified some aromatic intermediates. Finally, Abellán et al., [29] only reached 23% TOC degradation with 0.5 g L^{−1} TiO₂ and also found some aromatic intermediates. The photofenton process (UVA/Fe(II)/H₂O₂) was

^{*} Corresponding author. Tel.: +34 924289387; fax: +34 924289385.
E-mail address: fbeltran@unex.es (F.J. Beltrán).

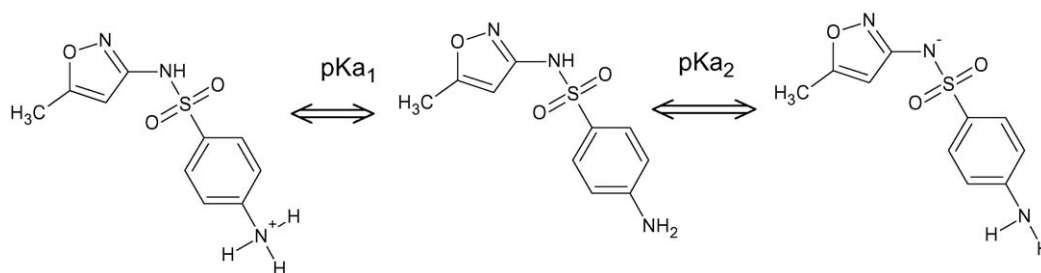


Fig. 1. Molecular structure and equilibrium of sulfamethoxazole in water ($pK_1 = 1.7$; $pK_2 = 5.6$).

also studied with the end of increase the biodegradability of SMX treated solutions [30]. The authors also observed about 80% TOC removal with 40 mEinstein L⁻¹ dose. Electrochemical oxidation with boron doped diamond anode to generate hydroxyl radicals has also been studied. In this case, high mineralization is achieved and some kinetics aspects are dealt with [31]. Some author of the present work has also studied the advanced oxidation of SMX with the combination between ozone and photocatalytic oxidation (O₃/UVA/TiO₂) that resulted in a high mineralization degree (70% TOC removal in 45 min) [32]. Also, the kinetics of the SMX and TOC photocatalytic ozonation was discussed and a kinetic model was proposed [22]. In summary, from these previous works, a fast reactivity of ozone with SMX is observed, the rate constants of the ozone and hydroxyl radical reactions with SMX have been determined and a variable mineralization degree is achieved that depends on the advanced oxidation process applied. However, in systems that allow a high mineralization, such as electrochemical oxidation or photocatalytic ozonation, the process is not cost effective and its real application is not yet feasible. At first sight, Heterogeneous catalytic ozonation does not present these drawbacks although much research is still needed. Therefore, this research group decided to study the combined effects of ozone and some alumina supported cobalt oxide and perovskite type as catalysts, on one hand, and activated carbons promoters, on the other hand to check the mineralization degree of SMX ozonated aqueous solutions. Also, the kinetics of the process is discussed to establish the kinetic regime of ozonation (importance of mass transfer versus chemical reactions) and get kinetic information for future process modeling.

2. Experimental

SMX was obtained from Sigma–Aldrich and used as received. Three commercial activated carbons and metal-based catalysts were selected or prepared to be used. Hydraffin P110, Darco 12–20, and GMI 2000 granular activated carbons with particle size in the range of 1–1.25 mm were obtained from Lurgy, Aldrich and Galaquim S.L., respectively. Previously to be used, the activated carbons were washed in boiling ultrapure water to remove possible impurities and thereupon dried out at 110 °C for 24 h. Cobalt supported alumina catalysts (Co/Al₂O₃) were prepared by the incipient wetness method [33]. This technique is commonly used in the preparation of heterogeneous catalysts. An aqueous solution containing the active metal precursor is added to the support in such a way as the volume of solution used is the same pore volume of the solid. Consequently the capillarity action leads the solution into the pores. For the preparation of the Co/Al₂O₃ catalysts, a solution with cobalt acetate tetrahydrate (Sigma–Aldrich) was used to impregnate 4 mm diameter commercial γ -Alumina (Alcoa Inc., USA). The impregnated samples were dried at 110 °C for 48 h before being calcined in air for 2 h at 800 °C. The copper type perovskite (LaTi_{0.15}Cu_{0.85}O₃) was obtained by citrate decomposition using the method described by Sotelo et al. [34]. So

that, 250 ml of a concentrated solution of La(NO₃)₃·6H₂O (20.6×10^{-3} M) was mixed with Cu(NO₃)₂·3H₂O with Cu:La ratio of 0.85. Subsequently after 1 h of strong agitation at 0 °C in a thermostatic bath containing ice, the source of titanium (titanium butoxide solution in isopropyl alcohol) was added slowly into the solution to achieve a Ti:La ratio of 0.15. Then, the exact stoichiometric amount of citrates as citric acid was introduced in the media to produce the corresponding metal complexes. The final pH of the final solution was between 2 and 3. The suspension formed was vigorously agitated during 2 h to favor the homogenization of the metallic citrates. Afterwards, the previous dispersion was dried at 100 °C for 24 h to remove nitrates and, finally, the resulting gel was calcined at 700 °C for 5 h. Likewise, cobalt type perovskite (LaTi_{0.15}Co_{0.85}O₃) was synthesized in the same way but using Co(NO₃)₂·3H₂O as a precursor of the metal. Catalysts and activated carbons were then characterized. Thus, adsorption of nitrogen at 77 K (Quantachrome Autosorb-1 automated gas adsorption system) and mercury porosimetry (Thermo Scientific Pascal 240 porosimeter device) were carried out for textural characterization while analysis of the surface oxygen groups concentration and determination of the point of zero charge, pH_{pzc}, were made for chemical surface characterization with the Boehm and Noh and Schawrz's methods, respectively [35,36]. Characteristics data of catalysts and activated carbons promoters are given in Table 1.

For the reactions carried out using granular activated carbons, a tubular glass reactor (300 mm long, 50 mm diameter) with a porous plate at the bottom of the reactor was used in series with a 30 mm long, 30 mm diameter packed bed column. The tubular reactor was used as ozonation chamber while the activated carbon laid down on the bed reactor. The aqueous solution was continuously recirculated at a flow rate of 2 L h⁻¹. More details can be seen in a previous work [13]. On the other hand, for the experiments performed using powered perovskite catalysts, the reactor employed was basically a 300 cm³ cylindrical glass vessel supplied with magnetic agitation, a diffuser plate at the bottom through which the ozone–oxygen gas mixture was continuously fed and a sampling port. In some cases the solutions were buffered at the desired pH in ultrapure water (Millipore Q Millipore system)

Table 1

Characterization properties of the catalysts and activated carbons used^a.

Catalyst	V_{mi} , cm ³ g ⁻¹	V_{me} , cm ³ g ⁻¹	S_{BET} , m ² g ⁻¹	pH _{pzc}
Darco 12–20	<0.286	>0.507	659.1	6.4
Hydraffin P110	0.455	0.111	950.3	9.7
GMI 2000	<0.334	>0.125	686.3	9.2
LaTi _{0.15} Co _{0.85} O ₃	0.0048	0.1231	13.26	
LaTi _{0.15} Cu _{0.85} O ₃	<0.0051	>0.0265	13.50	9.8
γ -Al ₂ O ₃	0.103	0.280	288	8.1
γ -Al ₂ O ₃ /Co (1%), $T_{calcination} = 800$ °C	0.076	0.303	209.6	8.5

^a V_{mi} , micropore volume; V_{me} , mesopore volume; S_{BET} , BET surface area; pH_{pzc} = point of zero charge.

with NaH_2PO_4 and Na_2HPO_4 and ionic strength of 0.05 M. Samples were withdrawn with a syringe from the reactor to be analyzed. The parent compound, TOC, hydrogen peroxide, carboxylic acids intermediates, dissolved ozone and absorbance at 254 nm were followed throughout the reaction. Prior the analysis the samples were filtered using 0.45 μm Millipore filters. Ozone was produced from oxygen in a Sander Laboratory Ozonator with gas flow rates ranging from 10 L h^{-1} to 25 L h^{-1} . Likewise ozone concentration on the gas flow was set at 20 mg L^{-1} .

Analytical methods to determine the concentrations of SMX, carboxylic acid type intermediates, hydrogen peroxide, ozone in water and in the gas phase and remaining organic carbon are described in detail in a previous paper [32].

3. Results and discussion

A series of experiments of SMX adsorption, ozonation and catalytic or promoted ozonation were first carried out for comparative reasons.

3.1. Adsorption of SMX on the catalyst and activated carbons used

Due to the importance of adsorption on the mechanism of catalytic advanced oxidation systems a first series of SMX adsorption experiments was carried out with the different catalysts and activated carbons used. Activated carbons, regardless of their nature, showed a strong affinity for SMX allowing total adsorption of this compound in about 60 min. On the contrary, alumina, cobalt oxide and perovskite type catalysts did not show or slightly showed adsorption affinity. Thus, perovskite type catalysts did not adsorb more than 1% SMX while only about 7% SMX was adsorbed on the alumina or cobalt oxide catalyst used after 2 h.

In addition, adsorption processes were also carried out at different pH between 2 and 9 in the presence of the activated carbons (ACs). The results (not shown), however, indicated no significant differences of SMX adsorption with pH for GMI 2000 and P110 Hydrafin ACs while a slightly positive influence of decreasing pH was observed when Darco AC was used. The effect of pH on the adsorption process can be better explained from isotherm results. In Fig. 2 SMX adsorption isotherms corresponding to SMX–Darco AC system at different pH are shown. It can be

observed that low pH values (between 2 and 5) lead to the highest SMX adsorption regardless of SMX equilibrium concentrations. Isotherms obtained from SMX adsorption on the other two AC used show similar results as far as the importance of low pH values is concerned, that is, with P110 Hydrafin and GMI 2000 ACs increasing SMX equilibrium affinity for ACs was noticed with decreasing pH. The results can be explained by considering the positive or negative charges on the surface of ACs and SMX molecule that highly depends on pH, pH_{pzc} of ACs and pKs of SMX equilibrium in water (pKs are 1.7 and 5.6 [21]). Thus, Darco AC presents a $\text{pH}_{\text{pzc}} = 6.3$ so that it is not surprising that adsorption at pH values 7 and 9 leads to the worst results considering the possible repulsive forces between the negatively charged AC surface and the anionic form of SMX. On the contrary, for $\text{pH} < \text{pH}_{\text{pzc}}$ (pH between 2 and 5) an important fraction of SMX is in neutral or anionic form and this could favor attractive electrostatic forces with the positively charged AC surface. For the other two ACs (GMI 2000 and P110 Hydrafin) corresponding pH_{pzc} are something higher than 9 so that decreasing the pH of water should favor SMX adsorption due to identical reasons than for SMX–Darco AC system.

For the case of alumina or cobalt oxide/alumina catalysts, the adsorption isotherm study was carried out at pH 3.3 (non-buffered system) and pH 7 (buffered system). The results (not shown) leads to SMX equilibrium adsorbed concentrations one order of magnitude lower than on ACs. In these cases, the presence of cobalt oxide exerted a little effect on isotherm results especially at pH 7. Also, the increase of pH leads to poorer adsorption results although this could likely be due to the competition of phosphates that show high affinity for alumina [37].

3.2. Catalytic or promoted ozonation of SMX

Once adsorption was studied, a series of catalytic or promoted ozonation experiments with the catalysts and activated carbons used, respectively, was carried out.

3.2.1. Evolution of SMX concentrations

First, the effect of catalytic-promoted ozonation was studied on the starting chemical SMX. Fig. 3 shows the changes of SMX concentrations with time of these experiments. These experiments

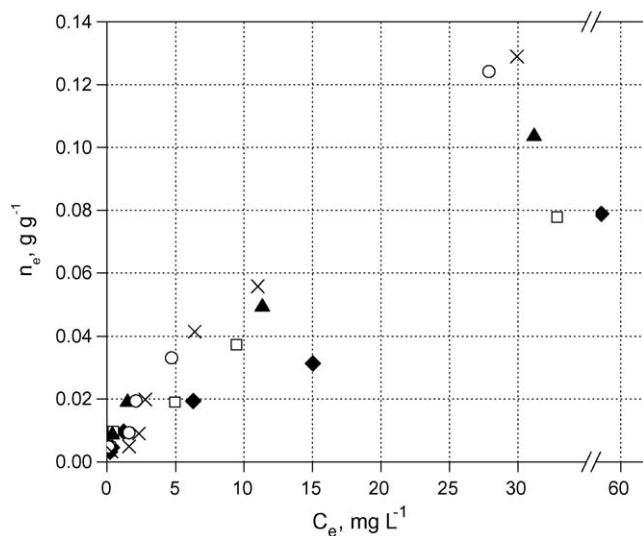


Fig. 2. Adsorption isotherms of SMX on Darco 12–20 AC. Conditions: initial SMX concentration, 100 mg L^{-1} ; $T = 20^\circ\text{C}$; \circ pH 2; \blacktriangle pH 5; \square pH 7; \blacklozenge pH 9; \times non-buffered SMX solution: pH 3.3.

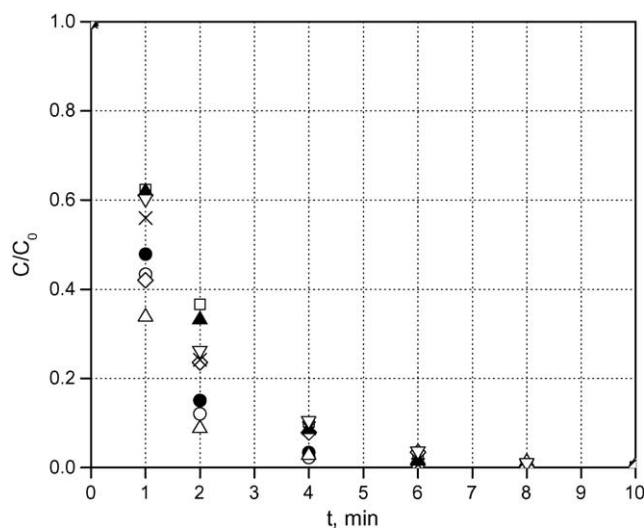


Fig. 3. Changes of SMX remaining concentration with time during ozonation in the presence and absence of catalyst or activated carbon promoters. Initial conditions, Initial SMX concentration = 30 mg L^{-1} ; $T = 20^\circ\text{C}$; ozone gas concentration = 20 mg L^{-1} ; pH 7; \square single ozonation; \bullet Darco 12–20; \triangle GMI 2000; \circ Hydrafin 110; \blacktriangle $\gamma\text{-Al}_2\text{O}_3$; ∇ $\text{Co/Al}_2\text{O}_3$; \diamond $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$; \times $\text{LaTi}_{0.15}\text{Co}_{0.85}\text{O}_3$.

were duplicated so that Fig. 3 shows average values of the concentrations. As it can be seen from Fig. 3 SMX is completely removed from the aqueous solution in 6–10 min. Also, it is seen that there are no significant differences between single ozonation and catalytic (alumina and cobalt oxide/alumina catalysts) ozonation results. However, SMX removal rates are something higher in activated carbon-promoted ozonation than in single ozonation, especially during the first three minutes of reaction. These differences are likely due to the sum of effects of direct ozonation and activated carbon adsorption as also checked in previous works with other pharmaceutical compounds such as diclofenac, of high AC adsorption affinity [13]. Discussion of these results first requires some considerations about the SMX direct reaction with ozone. In previous works [20–24] the rate constant of the ozone–SMX direct reaction was reported to be of the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ which means a fast gas–liquid reaction develops. The absence of dissolved ozone during the first minutes of ozonation (also observed in this work) confirmed this kinetic regime. At these conditions, nearly all SMX molecules should react with ozone in the liquid film close to the gas–liquid interface while a small SMX fraction is adsorbed on the activated carbon surface. Then, removal of SMX is due to the sum of the contributions of direct ozonation and physical adsorption. Removal of SMX when ozonated in the presence of the catalysts used confirms this statement. Thus, SMX removal rates in these processes and in single ozonation are practically coincident, that is, the results are exclusively due to direct ozone reactions since SMX hardly adsorbs on the catalyst surface. Thus, following the film theory concepts [38,39], on one hand, ozone, once dissolved in water, is totally depleted by reacting with SMX (and likely first unsaturated intermediates) in the liquid film close to the gas–water interface. On the other hand, some SMX is also eliminated by adsorption on the AC surface. Notice that ozone-promoted surface reactions cannot develop because ozone does not reach the liquid film close to the water–solid interface because of the fast gas–liquid kinetic regime of SMX ozonation. In the case of catalytic ozonation, the main loss of SMX concentration would only be noted through the liquid film close to the gas–liquid interface. Then, use of catalysts or promoters of ozone decomposition is not useful to remove SMX from water. However, a different situation is presented regarding saturated intermediates, measured as TOC, as presented below.

3.2.2. Evolution of total organic carbon

During SMX ozonations and regardless of the presence of catalysts or promoters both hydrogen peroxide and saturated carboxylic acids (pyruvic and oxalic acids) were detected and their concentrations measured. Also, absorbance measurements at 254 nm, which gives an estimation of the presence of aromatic compounds, continuously diminish with time. Figs. 4 and 5 present examples of this for the cases of single ozonation and Darco AC-promoted ozonation of SMX, respectively. As it is seen from Fig. 4 hydrogen peroxide concentration first increases, it reaches a maximum value and then diminishes with time to disappear after 2 h reaction. At the same time, during ozonation alone, pyruvic and oxalic acids also accumulate in water and only the concentration of the former slightly diminish with time (see Fig. 4). Similar results were obtained in the presence of the cobalt/alumina catalyst (not shown). In the presence of AC the concentration of the two carboxylic acid follow similar trends during the first 6–10 min of reactions and eventually diminish with reaction time, (see Fig. 5). For perovskite catalytic ozonation concentration trends of oxalic and pyruvic acids with time (not shown) were similar and of the same order of magnitude to those measured in the presence of activated carbons, that is, also in these cases, saturated carboxylic acids eventually disappear from water. Formation of hydrogen peroxide in ozonation processes is a well known step of the ozonation mechanism of unsaturated compounds due to the

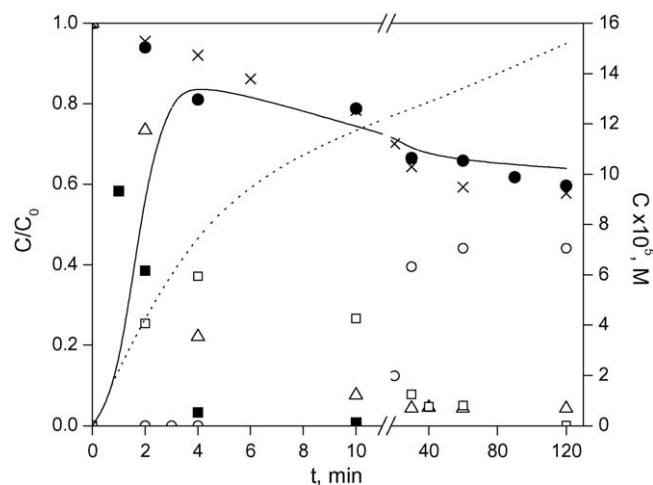


Fig. 4. Time evolution of dimensionless concentration of SMX, TOC and absorbance at 254 nm (left axis) and hydrogen peroxide, dissolved ozone, pyruvic and oxalic acid (right axis) in the SMX single ozonation. Conditions: initial TOC, 15 mg L^{-1} ; $T = 20^\circ \text{C}$; pH 7; liquid recirculation flow = 2 L h^{-1} ; ozone gas concentration = 20 mg L^{-1} ; gas flow rate = 25 L h^{-1} ; ● TOC; △ absorbance at 254 nm; ■ SMX; ○ dissolved ozone; □ hydrogen peroxide; solid line pyruvic acid; dotted line oxalic acid, x TOC for gas flow rate = 10 L h^{-1} .

aromatic ring or carbon atom double bonds breaking with ozone [39]. Also, in the presence of AC hydrogen peroxide is known to be formed due to ozone decomposition on the AC surface [40,41]. The results shown in Figs. 4 and 5 indicate that carboxylic acid formation practically develops since the start of ozonation while unsaturated compounds (i.e. aromatics and carboxylic acids with carbon double bonds) practically disappear after few minutes due to their fast reactions with ozone. Then, the organic matter present in water is mainly due to saturated organic compounds such as carboxylic acids. This is confirmed for reaction times higher than 40 min when the calculated TOC from pyruvic and oxalic acid concentrations represented, in the catalytic or promoted ozonations studied, more than 90% of the experimentally determined TOC. Because of its importance, total organic carbon evolution with time was followed during the ozonation experiments. Fig. 6 presents an example of this corresponding to experiments of

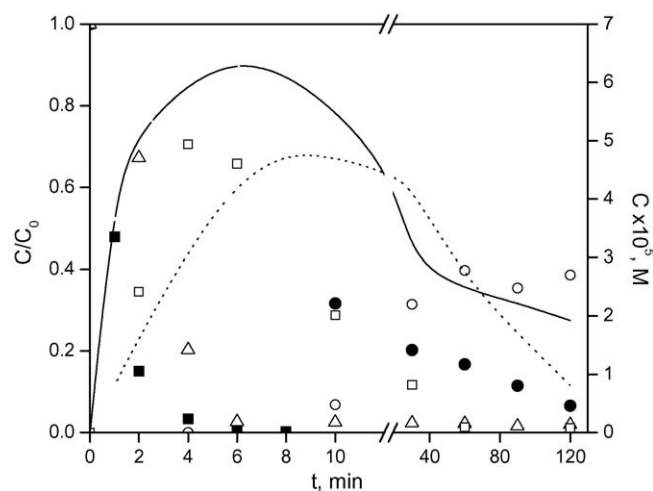


Fig. 5. Time evolution of dimensionless concentrations of SMX, TOC and absorbance at 254 nm (left axis) and hydrogen peroxide, dissolved ozone, pyruvic and oxalic acid (right axis) in SMX ozonation in the presence of Darco 12–20. Conditions: initial TOC, 15 mg L^{-1} ; $T = 20^\circ \text{C}$; pH 7; liquid recirculation flow = 2 L h^{-1} ; ozone gas concentration = 20 mg L^{-1} ; $Q = 25 \text{ L h}^{-1}$; ● TOC; △ absorbance at 254 nm; ■ SMX; ○ dissolved ozone; □ hydrogen peroxide; solid line pyruvic acid; dotted line oxalic acid.

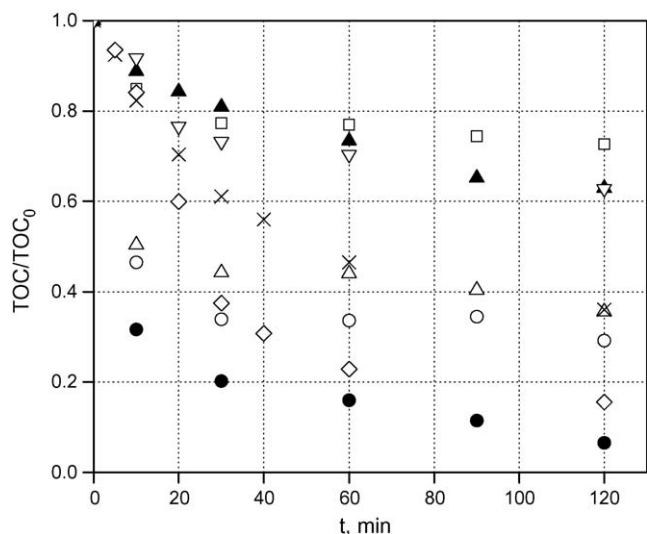


Fig. 6. Changes of TOC with time during ozonation of SMX in the presence and absence of catalysts or AC promoters. Initial conditions, $\text{TOC}_0 = 15 \text{ mg L}^{-1}$; $T = 20^\circ\text{C}$; ozone gas concentration = 20 mg L^{-1} ; pH 7; \square single ozonation; \bullet Darco 12-20; \triangle GMI 2000; \circ Hydruffin P110; \blacktriangle $\gamma\text{-Al}_2\text{O}_3$; ∇ $\text{Co/Al}_2\text{O}_3$; \diamond $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$; \times $\text{LaTi}_{0.15}\text{Co}_{0.85}\text{O}_3$.

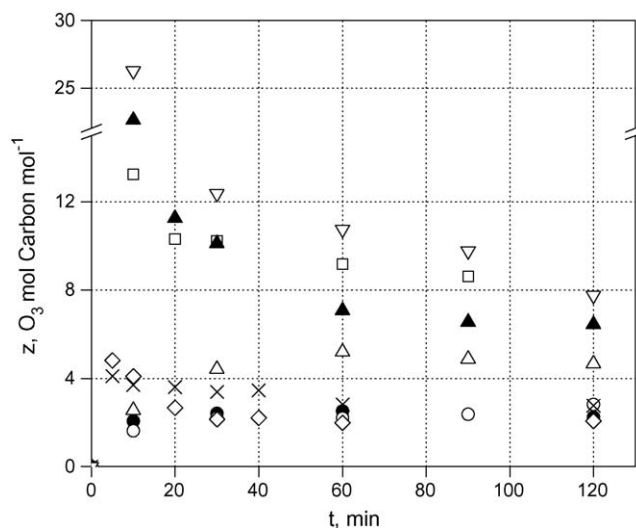


Fig. 7. Ozone consumption evolution with time in the catalytic or promoted ozonation of SMX. Initial conditions, $\text{TOC}_0 = 15 \text{ mg L}^{-1}$; $T = 20^\circ\text{C}$; ozone gas concentration = 20 mg L^{-1} ; pH 7; \square single ozonation; \bullet Darco 12-20; \triangle GMI 2000; \circ Hydruffin P110; \blacktriangle $\gamma\text{-Al}_2\text{O}_3$; ∇ $\text{Co/Al}_2\text{O}_3$; \diamond $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$; \times $\text{LaTi}_{0.15}\text{Co}_{0.85}\text{O}_3$.

catalytic-promoted ozonation of SMX. As it can be seen from Fig. 6 the use of catalyst or promoters activates TOC removal compared to the single ozonation process. However, significant differences can be observed depending on the nature of catalyst or promoter used. Thus, alumina or cobalt oxide/alumina catalysts slightly improve the mineralization compared to the single ozonation process (28% against 39% after 2 h). Also, the presence of cobalt oxide does not imply a better mineralization rate than that observed when alumina alone was used at pH 7. There is an abundant literature about the catalytic activity of alumina and metal–alumina in ozonation processes [37,42,43]. Both physical and chemical parameters of the catalyst have to be considered. Physical variables are specific surface area, pore volume, porosity, etc., and chemical properties are acidity and basicity that depend on the presence of hydroxyl groups directly related to the nature of the metal oxide. Thus, alumina can act as ion and ligand exchanger. In the present study, however, adsorption of organic intermediates is not important (see later Fig. 8) and ozone adsorption and decomposition to yield surface bound oxygen radicals or hydroxyl radicals as previously reported [42] is likely the main mechanism of oxidation. Extensive information about these reactions can be seen elsewhere [42,43]. In this work small differences are observed between the results obtained with alumina and cobalt/alumina catalysts, which suggests that most of catalytic active centers belong to the alumina surface.

Some different results are obtained when perovskite type catalysts or activated carbons are used. Thus, copper type perovskite and Darco AC are able to remove 85% and 92% TOC in 2 h, respectively, while the cobalt type perovskite and the other two activated carbons allow TOC removals between 60% and 70%. Contrary to the case of alumina, as far as our knowledge is concerned, there is no reported information on the activity of perovskite type catalysts on ozone processes. However, one possible mechanism explaining the activity of these catalysts is likely due to the ozone adsorption on the catalyst surface to yield superoxide ion species (through metal–ozone electron transfer) that eventually leads to hydrogen peroxide or also react with ozone to generate hydroxyl radicals as has been reported in studies on the heterogeneous catalytic ozone decomposition in gas phase [44].

Another important issue to measure the ozonation efficiency is the consumption of ozone per TOC removed. Values of this

parameter for the different ozonation systems studied are presented in Fig. 7 against reaction time. As it can be seen, Darco and Hydruffin P110 ACs and copper and cobalt type perovskites lead to the lowest ozone consumption values among catalysts and activated carbons used. Since Darco AC also leads to the highest TOC removal rates, herein, the ozonation study is focused on the use of perovskites and Darco AC.

Another important aspect to study refers to the adsorption affinity, for catalysts or promoters, of the organic matter resulting from SMX ozonation processes. Thus, in this work some adsorption kinetic experiments were carried out with SMX ozonated solutions. In Fig. 8 the changes of total organic carbon with time during the adsorption of an ozonated SMX aqueous solution are shown. It can be seen from Fig. 8 that the organic matter resulting for preozonation times ≥ 10 min hardly adsorbs on the AC carbon surface which is likely due to the polar nature of intermediates of the SMX ozonation. For lower preozonation times, however,

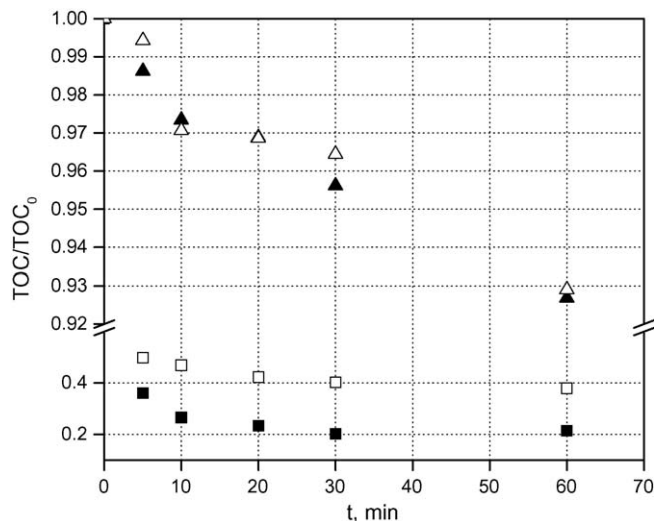


Fig. 8. Changes of TOC with time in the adsorption on Darco 12-20 AC of various SMX preozonated solutions during different reaction times. Initial concentration of SMX: 30 mg L^{-1} ; $T = 20^\circ\text{C}$; pH 7; $w = 20 \text{ g L}^{-1}$. Preozonation time: \blacksquare 1 min; \square 4 min; \blacktriangle 10 min; \triangle 30 min.

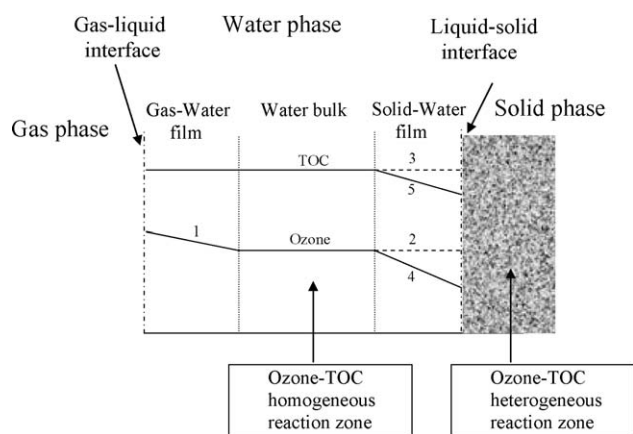


Fig. 9. Assumed concentration profiles for TOC and ozone in catalytic or activated carbon ozonation according to the film theory. 1: ozone depletion profile due to gas-liquid ozone mass transfer. 2 and 3: uniform ozone and SMX profiles, respectively, due to surface reaction control. 4 and 5: non-uniform ozone and SMX profiles, respectively, due to liquid-solid external mass transfer control.

intermediates (likely still unsaturated compounds as 254 nm absorbance measurements suggest) strongly adsorbs on the AC surface. This means that once SMX has disappeared (after at least 6 min ozonation as shown in Fig. 3) reactions of intermediates (mostly saturated compounds that do not react directly with ozone, see Figs. 4 and 5) will be removed through free radical reactions. Hydroxyl radicals of these reactions could be generated in three ways: from the hydroxyl ion catalyzed decomposition of ozone [45], from the ozone and hydrogen peroxide reaction in the water phase [46] and from the decomposition of ozone on the perovskite type catalysts and activated carbon promoter surfaces [9,40]. Fig. 9 shows, according to the film theory [38,39], the assumed TOC and ozone concentration profiles with the depth of water between liquid films closed to the gas-water and solid-water interfaces. As it is shown TOC depletion only occurs at the water bulk and at the proximity of the liquid solid interface due to the reactions with hydroxyl radicals formed from ozone-hydrogen peroxide reactions in water bulk and/or on the solid surface. Notice that the ozone depletion through the liquid film close to the gas-water interface is due to the mass transfer resistance. Also notice that the concentration profiles of TOC and ozone through the liquid-solid interface can be uniform (when surface reactions control the heterogeneous ozone reactions, see section 3.3.1) or non-uniform (when external diffusion controls the heterogeneous ozone reactions, see section 3.3.2).

3.2.3. Effect of pH

Water pH is one of the variables most affecting ozonation processes [47]. In the case of catalytic and AC-promoted ozonation processes an even more importance influence of pH can be expected due to its effects on charge distribution on the catalyst-promoter surface and on the rate of the reaction between ozone and hydrogen peroxide. Thus, some experiments of catalytic ozonation were also carried out at different pH. For these experiments only the evolution of TOC is discussed since SMX removal rates are nearly independent on pH (the direct rate constant of the SMX-ozone reaction varies between 2.65×10^5 and $4.65 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for pHs 2 and 9, respectively, [22]). Thus, Fig. 10 presents the changes of TOC with time corresponding to experiments of Darco AC ozonation at different pH, as example. As it is observed from Fig. 10 TOC removal rates for pH 2–7 are similar while for pH 9 some lower values are deduced. It seems that reactions involving ozone and hydrogen peroxide on the activated carbon surface to generate hydroxyl radicals are very important if not, a positive effect of pH on TOC removal rate should have been

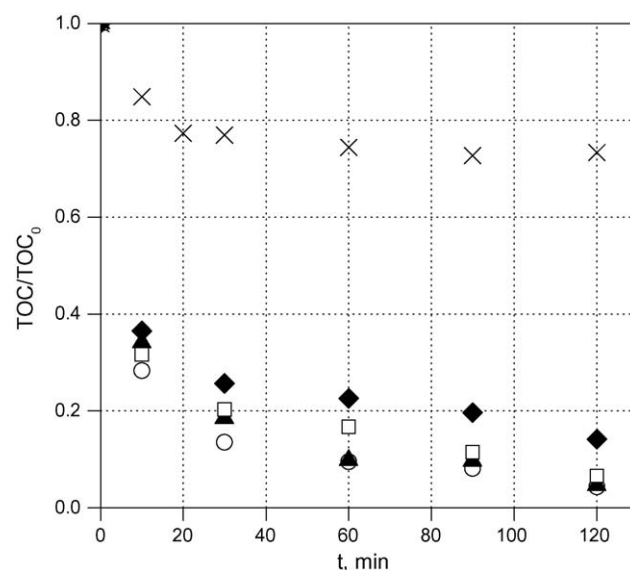


Fig. 10. Dimensionless evolution of TOC with time in SMX ozonation in the presence of Darco activated carbon at different pH. Initial concentration of sulfamethoxazole, 30 mg L^{-1} ; $T = 20^\circ \text{C}$; ozone gas concentration = 20 mg L^{-1} ; \circ pH 2; \blacktriangle pH 5; \square pH 7; \blacklozenge pH 9; \times single ozonation pH 7.

noted. It should be reminded that ACs are not true catalysts in ozonation processes because some of their basic oxygen surface groups react with ozone to yield hydrogen peroxide and more acidic oxygen surface groups (this is why ACs are called promoters). For example, untreated Darco AC has 196 and $165 \text{ } \mu\text{eq L}^{-1}$ of basic and carboxylic acids surface groups, respectively, while after ozonation at pH 7, basic groups reduce to $59 \text{ } \mu\text{eq L}^{-1}$ and carboxylic acid groups increase to $265 \text{ } \mu\text{eq L}^{-1}$. However, the loss of AC weight is negligible and its activity is kept constant, at least, after four consecutive ozonation experiments (not shown) where the same amount of activated carbon was used with fresh SMX aqueous solutions (this is why for kinetic study purposes AC is considered in this work as a catalyst of ozonation as is shown in section 3.3).

Considering the perovskite catalytic ozonation results at different pH (not shown), the decreasing pH leads to an increase of TOC removal but also to an increase of metal leaching (i.e. approximately 4.5 mg L^{-1} metal was leached after 2 h ozonation at pH 3.5). Thus, for this catalytic process, the increase of TOC removal is likely due to the homogeneous catalytic ozonation, that is, due to the presence of copper or cobalt ions in water. It is well known that these metals when present in the aqueous solutions considerably increase the ozonation rates of organic compounds [48,49]. At pH 7, however, no metal leaching was observed at all and, also, the activity of the perovskite catalyst, as far as TOC removal is concerned, kept constant after four consecutive uses. Then, perovskite catalytic ozonation should be limited to neutral pH where TOC degradation presents high efficiency (see Fig. 6).

3.3. Kinetics of ozonation processes

The kinetic study of the activated carbon or perovskite catalytic ozonation processes used in this work has then been focused on TOC elimination and it can be accomplished by considering the absorption rate equations of gas-liquid-solid catalytic reactions. TOC removal in these processes is due to the reactions with hydroxyl radicals that come from ozone and hydrogen peroxide reactions both on the bulk water and on the solid surface. Also, formation of hydrogen peroxide comes from ozone reactions with unsaturated compounds in bulk water and ozone decomposition on the solid surfaces. Thus, in any case, the rate of TOC reactions

should be proportional to the concentrations of ozone since both hydrogen peroxide and, then, hydroxyl radicals come from the ozone decomposition.

A mass balance of TOC in water in a semibatch well agitated reactor is:

$$-z \frac{d\text{TOC}}{dt} = N_{\text{O}_3} \quad (1)$$

where z and N_{O_3} are the stoichiometric ratio (consumption of ozone per mol TOC consumed) and the absorption rate of ozone in water, respectively, defined as follows [50]:

$$N_{\text{O}_3} = \frac{C_{\text{O}_3\text{g}}RT}{(\text{He}/k_{\text{La}}) + [\text{He}/\phi(k_{\text{H}}, \text{TOC}) + (w/(1/k_{\text{c}}a_{\text{c}}) + (1/\eta F(k_{\text{HET}}, \text{TOC})))]} \quad (2)$$

where $C_{\text{O}_3\text{g}}$ is the concentration of ozone in the gas, k_{La} and $k_{\text{c}}a_{\text{c}}$ the mass transfer coefficients in the liquid films close to the gas–water and water–solid interfaces, respectively, k_{H} and k_{HET} the rate constants of the homogeneous and heterogeneous ozone reactions in water and on the solid surface, respectively, He , R and η the Henry and gas perfect law constants and the internal effectiveness factor, respectively, T and w the temperature and concentration of catalyst or promoter and the inverse of $\phi(k_{\text{H}}, \text{TOC})$ and $F(k_{\text{HET}}, \text{TOC})$ are the homogeneous and heterogeneous chemical resistances of the process, respectively [51].

In the ozone processes studied a fraction of TOC reacts with ozone (or to better say with hydroxyl radicals coming from the ozone–hydrogen peroxide reaction in bulk water) which is called the homogeneous reaction. The kinetics of this reaction is first treated here. Thus, in the absence of catalyst or activated carbon, Eq. (2) reduces to the following one:

$$N_{\text{O}_3} = \frac{C_{\text{O}_3\text{g}}RT}{\text{He}/k_{\text{La}} + \text{He}/\phi(k_{\text{H}}, \text{TOC})} \quad (3)$$

In Eq. (3) the term He/k_{La} that refers to the liquid phase mass transfer resistance can be eliminated since ozonation experiments carried out at different gas flow rate lead to similar TOC removal rates (see Fig. 4). Then, the ozone process rate is exclusively of chemical control and Eq. (1) with the simplified Eq. (3) reduces to:

$$-z_{\text{H}} \frac{d\text{TOC}}{dt} = \frac{C_{\text{O}_3\text{g}}RT}{\text{He}} \phi(k_{\text{H}}, \text{TOC}) \quad (4)$$

where z_{H} is the stoichiometric ratio of the ozone–TOC homogeneous reaction that varies with time due to the different nature of intermediates formed. In ozone processes the term $\phi(k_{\text{H}}, \text{TOC})$ usually comes from a first order reaction with respect to TOC and ozone [39,52,53] so that it reduces to $k_{\text{H}}\text{TOC}$. Low integration limit of Eq. (4) corresponds to the time from which ozone reactions in bulk water are slow, which happens once SMX has nearly disappeared [22]. For practical purposes, it will be assumed that this reaction time, t_{i} , is the time of total disappearance of SMX (between 6 and 10 min, depending on ozonation process type as shown in Fig. 3). Notice that at this reaction time dissolved ozone starts to appear which confirms the slow kinetic regime of ozone absorption needed to apply Eqs. (2)–(4). With these assumptions, Eq. (4) after integration yields:

$$\ln\left(\frac{\text{TOC}_i}{\text{TOC}}\right) = k_{\text{H}} \frac{RT}{\text{He}} \lambda \quad (5)$$

where

$$\lambda = \int_{t_{\text{i}}}^t \frac{C_{\text{O}_3\text{g}}}{z_{\text{H}}} dt \quad (6)$$

Notice that $C_{\text{O}_3\text{g}}$ is the concentration of ozone in the gas leaving the reactor that varies with time because of perfect mixing

conditions. In Eq. (6), the stoichiometric ratio can be calculated with time as follows:

$$z_{\text{H}} = \frac{v_0 \int_{t_{\text{i}}}^t (C_{\text{O}_3\text{ge}} - C_{\text{O}_3\text{g}}) dt - C_{\text{O}_3} V}{V(\text{TOC}_i - \text{TOC})} \quad (7)$$

with v_0 , V , $C_{\text{O}_3\text{ge}}$ and C_{O_3} as the gas flow rate, reaction volume and concentrations of ozone in the feeding gas and in water, respectively. Fitting experimental data to Eq. (5) is shown Fig. 11. From the linear least squares analysis of the plotted lines, k_{H} was found to be 0.63 ± 0.01 , 0.81 ± 0.01 , 0.69 ± 0.01 and $1.49 \pm 0.21 \text{ M}^{-1} \text{ s}^{-1}$ at pH 2, 5, 7 and 9, respectively.

Known the homogeneous chemical resistance ($1/k_{\text{H}}\text{TOC}$), the kinetics of TOC removal in ozone processes with perovskite type catalysts and Darco activated carbon was then studied.

3.3.1. Kinetics of perovskite catalytic ozonation

Because perovskites were in powder form mass transfer resistances due to external diffusion through the liquid film close to the water–solid interface and internal diffusion are negligible so that the term $1/k_{\text{c}}a_{\text{c}}$ can be removed from Eq. (2) and the effectiveness factor reduces to unity [51,54]. With these simplifications and considering He/k_{La} also negligible, Eq. (2) becomes:

$$N_{\text{O}_3} = \frac{C_{\text{O}_3\text{g}}RT}{\text{He}} [k_{\text{H}}\text{TOC} + wF(k_{\text{HET}}, \text{TOC})] \quad (8)$$

Ozone–organics surface reactions can also be considered of first order with respect to both agents so that the term $F(k_{\text{HET}}, \text{TOC})$ becomes $k_{\text{HET}}\text{TOC}$. With this simplification in Eq. (8) TOC mass balance Eq. (1) is:

$$-z_{\text{T}} \frac{d\text{TOC}}{dt} = \frac{C_{\text{O}_3\text{g}}RT}{\text{He}} (k_{\text{H}} + wk_{\text{HET}})\text{TOC} \quad (9)$$

where z_{T} is now the stoichiometric ratio of the catalytic ozonation process that can also varies with time and can be calculated with Eq. (7). Integration of Eq. (9) also yields Eqs. (5) and (6) with $k_{\text{H}} + wk_{\text{HET}}$ and z_{T} instead of k_{H} and z_{H} , respectively. Fitting experimental data of the copper or cobalt perovskite catalytic ozonation process at pH 7 (when no metal leaching is observed) leads to $k_{\text{HET}} = 206 \pm 5$ and $290 \pm 5 \text{ L M}^{-1} \text{ g}^{-1} \text{ s}^{-1}$, respectively.

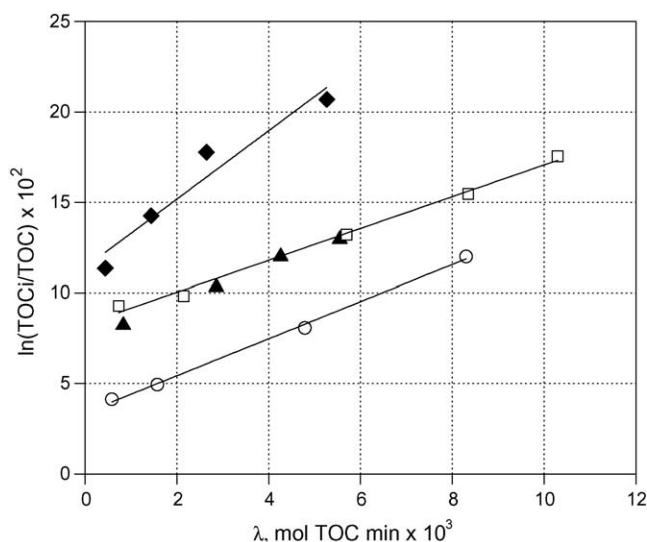


Fig. 11. Determination of the homogenous apparent rate constants of the mineralization of a sulfamethoxazole aqueous solution with ozone. Initial conditions, $\text{TOC}_i = 13 \text{ mg L}^{-1}$; $T = 20^\circ \text{C}$; ozone gas concentration = 20 mg L^{-1} ; \circ pH 2; \blacktriangle pH 5; \square pH 7; \blacklozenge pH 9.

Table 2

Mears criteria for SMX ozonation in the presence of Darco 12–20 activated carbon.

t, min	MC for TOC	MC for ozone
10	2.27	394.04
30	0.33	9.31
60	0.17	3.28
90	0.29	4.00
120	0.48	3.35

3.3.2. Kinetics of Darco activated carbon ozonation

Darco AC is not exactly a catalyst of the ozonation process but a promoter [9,12,55] since its surface reacts with ozone to yield hydrogen peroxide and, eventually, hydroxyl radicals. However, for practical purposes the amount of AC consumed with ozone is negligible. Thus, the kinetics of a gas–liquid–solid catalytic reaction, that is, Eq. (2), has also being applied to this case. Since Darco activated carbon particles were of 1 mm diameter, external diffusion likely controls the process rate [54]. Thus, Eq. (2) now becomes:

$$N_{O_3} = \frac{C_{O_3} RT}{He} [k_H TOC + wk_c a_c] \quad (10)$$

Substitution of Eq. (10) into Eq. (1), after variable separation and integration, yields:

$$\ln \frac{k_H TOC_i + wk_c a_c}{k_H TOC + wk_c a_c} = k_H \frac{RT}{He} \int_{t_i}^t \frac{C_{O_3}}{z_T} dt \quad (11)$$

Eq. (11) was solved by guessing the value of $k_c a_c$ that best fitted the experimental results. This value was found to be $4.3 \times 10^{-8} \text{ m}^3 \text{ g}^{-1} \text{ s}^{-1}$. With this $k_c a_c$ value a plot of the left side against the right side of Eq. (11) leads to a straight line of slope unity that goes through the coordinates origin (not shown) with a correlation coefficient of 0.995. To confirm the assumption of external diffusion control, the Mears Criteria (MC) [56] was applied. MC compares the relative importance of external diffusion rate to solid particles with the internal diffusion plus surface chemical reaction rate in a gas–liquid–solid catalytic reaction. MC applied to both TOC and ozone external diffusions can be defined as follows:

$$\text{For TOC diffusion : MC} = \frac{-dTOC/dt}{k_c a_c w TOC} \quad (12)$$

$$\text{For ozone diffusion : MC} = \frac{-z_T dTOC/dt}{k_c a_c w C_{O_3}} \quad (13)$$

Values of MC at different reaction times are given in Table 2. As can be seen MC values for both TOC and, especially, ozone diffusion are higher than 0.1 which confirms the assumption that external diffusion controls the process rate during Darco AC ozonation.

4. Conclusions

Major conclusions reached in the study of the SMX catalytic or promoted ozonation are:

- The use of combined ozone systems only slightly increases, in some cases (when activated carbons are used), the removal rate of SMX compared to ozonation alone. As a consequence, catalytic or promoted ozonation are not necessary to eliminate SMX from water in an ozonation process. However, for the removal of resulting TOC the combined ozone processes are recommended.
- Hydrogen peroxide and saturated carboxylic acids are intermediates found in single and catalytic-promoted ozonation of SMX. First intermediates are, however, unsaturated compounds that rapidly disappear from water as a result of direct ozone reactions.

- Saturated carboxylic acids intermediates are eliminated through hydroxyl radical oxidation. These reactions are significantly improved with the use of catalysts or activated carbons.
- In these processes, low pH has a negative effect when perovskite type catalysts are used because of metal leaching. In the case of activated carbons, the decreasing pH leads to better TOC removal rates likely due to the formation of hydroxyl radicals from ozone–hydrogen peroxide reactions on the activated carbon surface.
- Copper perovskite catalyst and Darco activated carbon resulted to be the most appropriate materials to improve TOC removal.
- Chemical reactions (homogeneous and heterogeneous) control the ozonation rate in the case of perovskite catalytic ozonation while external diffusion to solid particles was the controlling step in the case of Darco activated carbon ozonation.
- At pH 7, apparent homogeneous and heterogeneous reaction rate constants of perovskite ozonation were found to be 0.69 min^{-1} and $206 \text{ L M}^{-1} \text{ g}^{-1} \text{ min}^{-1}$, respectively.

Acknowledgements

This work has been supported by the CICYT of Spain and the European Region Development Funds of the European Commission (Project CTQ2006/04745). Mr. Pocostales also thanks the Spanish Ministry of Science and Education for a FPU grant.

References

- [1] B. Halling-Sørensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jørgensen, *Chemosphere* 36 (1998) 357–393.
- [2] K. Ikehata, N.J. Naghashkar, M.G. El-Din, *Ozone Sci. Eng.* 28 (2006) 353–414.
- [3] I. Gültekin, N.H. Ince, J. Environ. Manage. 85 (2007) 816–832.
- [4] T.E. Agustina, H.M. Ang, V.K. Vareek, J. Photochem. Photobiol. C Photochem. Rev. 6 (2005) 264–273.
- [5] I. Udrea, C. Badru, *Ozone Sci. Eng.* 25 (2003) 343–355.
- [6] Y. Pi, M. Ernst, J.C. Schrotter, *Ozone Sci. Eng.* 25 (2003) 393–397.
- [7] F.J. Rivas, M. Carbajo, F.J. Beltrán, B. Acedo, O. Gimeno, *Appl. Catal. B: Environ.* 62 (2006) 93–103.
- [8] M. Carbajo, F.J. Beltrán, O. Gimeno, B. Acedo, F.J. Rivas, *Appl. Catal. B Environ.* 74 (2007) 203–210.
- [9] M. Sanchez-Polo, U. von Gunten, J. Rivera-Utrilla, *Water Res.* 39 (2005) 3189–3198.
- [10] M. Sanchez-Polo, J. Rivera-Utrilla, *Appl. Catal. B Environ.* 67 (2006) 113–120.
- [11] H. Valdés, C.A. Zaror, *Chemosphere* 65 (2006) 1131–1136.
- [12] P.C.C. Faria, J.J.M. Orfao, M.F.R. Pereira, *Chemosphere* 67 (2007) 809–815.
- [13] F.J. Beltrán, P. Pocostales, P.M. Alvarez, A. Oropesa, J. Hazard. Mater. 163 (2009) 766–768.
- [14] X. Li, Q. Zhang, L. Tang, P. Lu, F. Sun, L. Li, J. Hazard. Mater. 163 (2009) 115–120.
- [15] N. Nakada, H. Shinohara, A. Murata, K. Kiri, S. Managaki, N. Sato, H. Takada, *Water Res.* 41 (2007) 4373–4382.
- [16] A.J. Watkinson, E.J. Murby, S.D. Costanzo, *Water Res.* 41 (2007) 4164–4176.
- [17] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, *Water Res.* 41 (2007) 1013–1021.
- [18] T.A. Ternes, J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann, B. Teiser, *Water Res.* 37 (2003) 1976–1982.
- [19] M.M. Huber, A. Göbel, A. Joss, N. Herrmann, D. Löffler, C.S. McArdell, A. Ried, H. Siegrist, T.A. Ternes, U. Von Gunten, *Environ. Sci. Technol.* 39 (2005) 4290–4299.
- [20] M.M. Huber, S. Canonica, G.Y. Park, U. von Gunten, *Environ. Sci. Technol.* 37 (2003) 5177–5186.
- [21] M.C. Dodd, M. Buffle, U. von Gunten, *Environ. Sci. Technol.* 40 (2006) 1969–1977.
- [22] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, *Water Res.* 43 (2009) 1359–1369.
- [23] M.C. Dodd, H.E. Kholer, U. von Gunten, *Environ. Sci. Technol.* 43 (2009) 2498–2504.
- [24] R.F. Dantas, S. Contreras, C. Sans, S. Esplugas, J. Hazard. Mater. 150 (2008) 790–794.
- [25] A.L. Boreen, W.A. Arnold, K. McNeill, *Environ. Sci. Technol.* 38 (2004) 3033–3940.
- [26] S.P. Mezyk, T.J. Neubauer, W.J. Cooper, J.R. Peller, J. Phys. Chem. A 111 (2007) 9019–9024.
- [27] R. Andreozzi, L. Campanella, B. Frayssie, J. Garric, A. Gonnella, R. Lo Giudice, R. Marotta, G. Pinto, A. Pollio, *Water Sci. Technol.* 50 (2004) 23–28.
- [28] L. Hu, P.M. Flanders, P.L. Miller, T.J. Strathmann, *Water Res.* 41 (2007) 2612–2626.
- [29] M.N. Abellán, B. Bayarri, J. Gimenez, J. Costa, *Appl. Catal. B Environ.* 74 (2007) 233–241.
- [30] O. Gonzalez, C. Sans, S. Esplugas, J. Hazard. Mater. 146 (2007) 459–464.
- [31] S. Li, D. Bejan, M.S. McDowell, N.J. Bunce, J. Appl. Electrochem. 38 (2008) 151–159.
- [32] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, A. Oropesa, *Water Res.* 42 (2008) 3799–3808.

- [33] C.N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, Inc., New York, 1980.
- [34] J.L. Sotelo, G. Ovejero, F. Martínez, J.A. Melero, A. Milieni, *Appl. Catal. B Environ.* 47 (2004) 81–294.
- [35] H.P. Boehm, *Adv. Catal.* 16 (1966) 179–184.
- [36] J.S. Noh, J.A. Schwarz, *J. Colloid. Interf. Sci.* 130 (1989) 157–162.
- [37] M. Ernst, F. Lurot, J.C. Schrotter, *Appl. Catal. B Environ.* 47 (2004) 15–23.
- [38] J.C. Charpentier, in: T.B. Drew, G.R. Cokelet, J.W. Hoopes, Jr., T. Vermeulen (Eds.), *Advances in Chemical Engineering*, vol. 11, Academic Press, New York, 1981, pp. 3–133.
- [39] F.J. Beltrán, *Ozone Reaction Kinetics for Water and Wastewater Systems*, Lewis Publishers, Boca Ratón, Florida, 2004.
- [40] J. Rivera-Utrilla, M. Sánchez-Polo, *Appl. Catal. B Environ.* 39 (2002) 319–329.
- [41] F.J. Beltrán, J.F. García-Araya, I. Giráldez, *Appl. Catal. B Environ.* 63 (2006) 249–259.
- [42] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, *Appl. Catal. B Environ.* 46 (2003) 639–669.
- [43] N. Karpel vel Leitner, H. Fu, *Top. Catal.* 33 (2005) 249–256.
- [44] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, *J. Phys. Chem.* 99 (1994) 10294–10299.
- [45] S. Staehelin, J. Hoigné, *Environ. Sci. Technol.* 19 (1985) 1206–1212.
- [46] S. Staehelin, J. Hoigné, *Environ. Sci. Technol.* 16 (1982) 666–681.
- [47] J. Hoigné, in: J. Hrubec (Ed.), *The Handbook of Environmental Chemistry. Part C Quality and Treatment of Drinking Water*, vol. 5, Springer-Verlag, Berlin Heidelberg, 1998.
- [48] G.R. Hill, *J. Am. Chem. Soc.* 71 (1949) 2434–2435.
- [49] M.S.E. Abdo, H. Shaban, M.S.H. Bader, *J. Environ. Sci. Health A23* (1986) 697–710.
- [50] P.A. Ramachandran, R.V. Chaudhari, *AIChE J.* 26 (1980) 177–201.
- [51] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd edition, Prentice-Hall, Englewood Cliffs, New Jersey, 1999.
- [52] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 173–183.
- [53] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 185–194.
- [54] C.N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, Robert E. Krieger Publisher Co. Inc., Malabar, FL, 1981.
- [55] U. Jans, J. Hoigné, *Ozone Sci. Eng.* 20 (1998) 67–89.
- [56] D.E. Mears, *Ind. Eng. Chem. Proc. Des. Dev.* 10 (1971) 541–547.